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(54) PRESSURE SENSITIVE ADHESIVE TAPE

(71) We, JOHNS-MANVILLE CORPORATION, a corporation organized under the laws of the State of New York, United States of America, of 22 East 40th Street, New York 16, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is directed to a pressure sensitive adhesive tape having both a high level of holding power and shear strength, and of adhesion and tack.

In many instances where pressure sensitive tape is used, a high order of adhesion, tack, shear strength, and holding power are all desirable properties. These properties are dependent upon the adhesive applied to the tape. It previously has not been possible to obtain a desirably high order of all these properties on one pressure sensitive tape. Generally a pressure sensitive tape with excellent adhesion and tack will be deficient in holding power and shear strength, whereas an adhesive with superior shear strength will not have superior tack and adhesion.

Accordingly, components which improve the holding power and the shear strength simultaneously normally have an adverse effect on the tack and adhesive properties of an adhesive composition of a pressure sensitive tape. Similarly, those components which improve the tack and adhesive properties simultaneously normally cause a substantial reduction in holding power and shear strength of a pressure sensitive adhesive. A typical example of this is an adhesive composition for pressure sensitive adhesive tapes, in which the composition includes a "resin" of one sort or another; in order to impart a high degree of holding power and shear strength, a resin having a relatively high melting point would be employed. However, when employing such a resin, having a high melting point, the tack and adhesiveness of the adhesive composition to be used on a pressure sensitive tape normally are substantially reduced, whereby it becomes much more important and critical to employ a select elastomer having a sufficiently high degree of adhesiveness and tackiness to compensate for the loss of tack caused by the employment of the high melting point resin. Similarly, if an elastomer having a low degree of tack is employed, in order to compensate and to have a satisfactorily high degree of adhesiveness and tack, it is necessary to employ a resin having a low melting point. However by employing the resin having a low melting point, the pressure sensitive adhesive tape normally will not have a desired high degree of holding power and shear strength.

Thus, there was a major problem in trying to produce a pressure sensitive tape desirably having a high level of each of holding power, shear strength, adhesion, and tack.

Another unsuccessful approach which has been attempted in an effort to overcome the problem is the employment of a random curing agent. By the employment of a curing agent, a composition may be partially cured whereby normally as the partial cure is increased in degree up to a point, adhesiveness increases but tack decreases; after passing a particular point in the partial cure, as cure conttinues to increase in degree, both the adhesiveness and tack de-

crease. Accordingly, although by the employment of a curing agent in order to accomplish a partial cure there may be obtained an increase in adhesiveness, for example in a composition having both a high melting point resin and an elastomer of low adhesiveness and tack, there remains the problem of an insufficient amount of tack for a desirable pressure sensitive tape. Also, in efforts to overcome the problem, additional failures proved that diverse random curing agents do not always work nor obtain uniform results, in respect of holding power and shear strength. For example, it was found that there is not always an increase in holding power and shear strength when a mere random conventional curing agent is employed.

Additionally, when various random curing agents are employed, there often are new problems introduced, such as staining as for example often results when sulfur is employed as a curing agent; the staining results on the material to which the pressure sensitive adhesive is attached.

Accordingly, the use of curing agents do not solve the problems discussed above, and in fact often raise merely new variables and new problems.

Another problem to which this invention is directed arises from the employment of a particular preferred backing tape for pressure sensitive adhesive tapes, namely, a vinyl backing tape. For any prior art composition which employed an isocyanate component, it had been found impossible to employ an aliphatic diluent with an isocyanate component because the aliphatic diluent caused the isocyanate to precipitate out of solution (and/or dispersion). It was therefore believed necessary to employ solely an aromatic diluent in combination with an isocyanate. However, it was also discovered that an aromatic diluent cannot be employed to treat a vinyl film because an aromatic solution degrades a vinyl film, for example, by penetrating the film, and typically causing swells, curls, and wrinkles in the film. Therefore, there apaprently exists no suitable adhesive solvent for an adhesive composition containing an isocyanate, to be applied specifically to a vinyl backing tape.

Also, in additional unsuccessful attempts to solve the problem, it was found that particularly the property of holding power of a pressure sensitive tape (as typically measured as the duration during which the tape will hold while under a constant stress tending to pull the tape from the object to which it is adhered) is subject to major detrimental effects resulting from the incorporation (by milling) of a filler component which in the conventional adhesive composition would be considered to be inert and which incorporation by milling for the conventional composition would be considered to be non-detrimental to the properties of a conventional adhesiv composition. For example, as is discussed more fully below, for the present invention it has been found that aluminum hydrate milled-in as a filler in the adhesive compositions of this invention has a major adverse and detrimental effect on the high holding power of the pressure sensitive adhesive composition of this invention.

This invention provides a pressure sensitive adhesive tape comprising a backing tape having coated on at least one face thereof an adhesive composition comprising an elastomer having a viscosity of from 40—100 Mooney, and a resinous composition including a major amount of high melting point resin melting at least above 105°C and a minor amount of a low melting point resin melting at least below 75°C wherein there is included from ½—5% of an isocyanate based on the weight of the elastomer, the ratio of the high melting point resin to the low melting point resin being from 8/1 to 3/1, and the adhesive composition is substantially free of a material highly reactive with the isocyanate, and a filler.

In preferred embodiments, the adhesive composition consists essentially of the above stated ingredients, and the elastomer has a preferred viscosity of 50 to 90 Mooney.

The process for producing the pressure sensitive tape of this invention comprises adding the isocyanate to a composition comprising an elastomer and a tackifier resinous composition present in an amount ranging up to 105 parts per 100 parts of elastomer by weight, and employing the isocyanate-modified composition as a pressure-sensitive adhesive on at least one side of a backing tape, whereby a pressure sensitive adhesive tape results characterized by substantialy improved holding power and shear strength without a substantial loss of adhesion and tack.

Another embodiment of this invention uses a solution of the above-described adhesive composition in an aliphatic solvent such as hexane and/or heptane, and the like, applied to a vinyl tape, such as plasticized polyvinyl chloride laminated with glass strands, for example. It was unexpectedly discovered that for the above-described adhesive composition, the isocyanate did not precipitate even though an aliphatic solvent was employed.

In the practice of the invention, the composition is dispersed in a diluent, preferably an aliphatic solvent, and in the form of a thick but flowable dispersion is typically applied to a face of the backing tape.

Preferably the resinous composition is selected from a group consisting of a ter-

pene resin comprising a major amount of pinene resin, a petroleum-derived resin, and a resin derived from hydrogenated wood rosin, and ranges from 80 parts to 95 parts of resin per 100 parts of the elastomer. Of these resins, the preferred resin is a terpene resin having a major amount of polymers of betapinene.

Preferably the high-melting point resin melts at a temperature at least above 110 degrees Centigrade, and has a weight ratio to the low-melting-point resin ranging from 8:1 to 3:1. A more preferred ratio ranges from 6:1 to 4:1.

Typical and representative isocyanate compositions for the above invention include methylene-bis-(4-phenyl isocyanate), toluene-2-4-diisocyanate, polymethylene polphenyl isocyanate, and the like. The adhesive composition of this invention employs any conventional elastomer provided that it either inherently has or has been otherwise adjusted (such as by milling) to a viscosity of 40 to 100 Mooney. However, because of the isocyanate and resinous composition of the adhesive composition, as discussed hereinbefore the adhesive composition has the improved holding power and shear strength while concurrently having the high level of tackiness and of adhesion, and it is not necessary to select merely those elastomers having the low melting point in order to retain the high level of tackiness. Accordingly, typical and representative elastomers include copolymers of butadiene and styrene (such as having a ratio of 77:23—known as GRS 1022), butyl acrylate:acrylonitrile polymer (such as 88:12 butyl acrylate:acrylonitrile copolymer), butadiene:acrylonitrile copolymer, natural rubber, pale crepe rubber, the ratios referred to being by weight. In a preferred embodiment, at least a major amount of the elastomer is the pale crepe rubber.

The backing tape preferably is either an acetate film or a vinyl film; however, other films which may be suitably employed within the scope of this invention broadly include paper, cloth, and film materials. Representative of these are paper, cotton textile material, paper or cotton textile material impregnated with a latex such as for example a polyurethane or a butadiene-acrylonitrile polymer modified by a butadiene-styrene polymer. Any one or more of these tapes may include conventional backing in a laminated form, employing backing materials such as fiber glass or rayon. Similarly, the backing film of this invention may include any convenient anchor layer for bonding such as is, for example, disclosed in U.S. Patent No. 2,555,745, in which an unvulcanized rubber plastic of diene polymer type, which may be either natural or a synthetic rubber, together with a minor portion of a compound such as methylene-bis-(4-phenyl-isocyanate) is employed. Another typical bonding agent is disclosed in U.S. Patent No. 3,075,853 and includes an aqueous or non-aqueous solvent media such as hydroxylic glutinous material in admixture with latices of hydrophobic elastomers or solvated elastomers with or without diisocyanate or alkyl titanates as disclosed in U.S. Patent Nos. 2,177,627 and 2,912,348, for example.

The adhesive composition may additionally include other conventional materials such as antioxidants, accelerators and reinforcing agents, provided that during their incorporation the elastomer viscosity is not reduced below the approximate minimum of about 40 Mooney. Typically representative fillers include zinc oxide, calcium carbonate, antioxidants, antiozononants and aluminum hydrate. However, as discussed above the holding power of the adhesive composition of the pressure sensitive tape of this invention is adversely affected to a major degree by the milled-incorporation of filler such as aluminum hydrate. This is unexpected in view of the fact that aluminum hydrate is normally considered not to be deleterious for random adhesive compositions. Therefore, this invention preferably excludes the milled-incorporation of aluminum hydrate. There is no known reason why milling-in aluminum hydrate should substantially reduce the duration of holding for the pressure sensitive tape of this invention, but the fact has nevertheless been substantiated experimentally. Similarly the adhesive composition excludes any substantial amount of a material highly reactive with the isocyanate additive of this invention.

It is significant to note that although one might presume the action of the isocyanate additive of this invention to be a "curing" action, there is evidence which raises questions as to the validity of such a theory. For example, as discussed above, normally additional cure adversely affects the formerly good adhesion and tack of a composition. Also, a series of curing catalysts were tried and resulted in failures prior to the discovery of the isocyanate additive of this invention.

Another typical disclosure of a film having additional bonding layers between the film and the pressure sensitive adhesive is U.S. Patent 3,085,903, in which an amine primary layer is adjacent to a non-fibrous film backing, and a polyfunctional isocyanate-elastomer mixture is located between the amine primary layer and the pressure sensitive adhesive layer.

A preferred pressure sensitive adhesive of this invention is a vinyl (such as polyvinyl chloride) film of about 2.5 mils thickness having about 52 ends of glass strand

reinforcement per inch applied in a laminate form. Another preferred embodiment includes about 60 ends of glass strand reinforcement on a vinyl film such as plasticized polyvinyl chlorid film. In another preferred embodiment, an acetate film of about 1.25 mils is reinforced with about 60 ends per inch of glass strand. The coating composition applied to each of these is disclosed in the following Table I.

TABLE I

Pounds	Ounces	Material	Supplier	Chem. Composition
245	0	1X Thin Pale Crepe	A. L. Grant Co.	
2	8	"SANTOVAR" A (Registered Trade Mark)	Monsanto Chem.	2,5 Ditert. —amyl— hydroquinone
210	0	"PICCOLYTE" (Registered Trade Mark) S115 #5115 Resin	Penn Indus. Chem. Co.	Hydrocarbon Terpene Resin composed of pinene, mainly Betapinene
35	0	"PICCOLYTE" (Registered Trade Mark) S70	Schenectady— Penn Indus. Chem. Co.	" "
480	0	Hexane	Chem. By-Prod. Drake Petroleum	
480	0	Heptane	" "	
24	0	"HYLENE" (Registered Trade Mark) M—50	DuPont	Methylene-bis-4 phenyl isocyanate dissolved in orthodichloro-benzene

In this composition the PICCOLYTE (Registered Trade Mark) S115 formed the high melting point resin and the PICCOLYTE (Registered Trade Mark) S70 formed the low melting point resin. The above representative formulation of the novel pressure sensitive tape of this invention includes the solvents hexane, and heptane. However, for the broad invention, any conventional organic solvent such as toluene, tetrahydrofuran, acetone, and the like may be employed.

Other representative conventional agents normally employed include, 2,5 ditertiary-amyl-hydroquinone ("SANTOVAR" Registered Trade Mark A), 2,6-ditertiary-butyl-4-methyl-phenol (i.e. "IONOL (Registered Trade Mark) Shell Chemical Corp.), lecithin, ("CLEARATE" B70 L, W. A. Cleary Corp.).

It should be noted that although as with any adhesive composition, the varying of proportions naturally has a definite effect on the overall properties of the composition, the percentage of elastomer in the adhesive formulation of this invention, the percentage of resinous material, and the like, do not have any more bearing on the overall properties of the composition in combination with the film for purposes of this invention than do varying percentages of prior art compositions, except to the extent already discussed above. Accordingly, the various ranges of percentages of the elastomer, the resinous material, and the other components may be varied to approximately the same extent that corresponding substantially similar prior art compositions may be varied without a substantial effect on the adhesive properties of the composition. However, as noted above, in the typical and representative adhesive formulation of Table I, the ingredients may be present in the approximate relative amounts disclosed in that formulation.

EXAMPLE I

In a test of holding power, a series of three separate adhesive compositions were prepared from a common batch, and each of the three adhesive compositions were applied to two separate but identical backing tapes, resulting in six separate pressure sensitive adhesive tapes one inch long and 0.5 inch wide. Each tape was uniformly adhered to an identical clean stainless steel plate surface and placed under one kilogram of applied weight to determine the length of time each would hold before coming loose as a result of the stress.

The pair of Group I pressure sensitive adhesive tapes each had an adhesive composition which consisted of pale crepe at 32 parts by weight, 31 parts of "PICCOLYTE" (Registered Trade Mark) S—115 (polyterpene resin melting at 115 degrees), 10 parts of "PICCOLYTE" (Registered Trade Mark)

S—70 (polyterpene resin melting at 70 degree), one part of "SANTOVAR" (Registered Trade Mark) A (ditertiary amyl hydroquinone), one part of "IONAL" (Registered Trade Mark) (2,6-ditertiary-butyl-4-methyl phenol), 1.5 part of TDI (toluene diisocyanate), 115 parts of each of heptane and hexane. This Group I composition is representative of a preferred embodiment of this invention.

The Group II composition includes the identical components and numbers of parts thereof, plus 18 parts of aluminum hydrate milled into the elastomer.

The Group III composition includes the same components and number of parts thereof as II, plus two parts of CKR 1634 resin (an oil-soluble heat-reactive para-terbutylphenylformaldehyde resin) and three parts of "VERSENE" (Registered Trade Mark) 67 (Dow Chemical Co.; sodium salt of ethylenediamine-tetracetic acid dihydrate), and one part of lecithin.

It should be noted that the Group I adhesive differed from the Group II and III adhesive in that the latter two required milling of the crepe rubber in order to mill-in the aluminum hydrate. The milling reduced the viscosity of each of II and III from 80 to 30 Mooney.

The period of holding power is shown in the following Table II.

TABLE II

Group	Hrs. Duration of Holding Power Sample (1)	Sample (2)
I	192(+)	192(+)
II	0.33	1.42
III	3.25	8.00

EXAMPLE II

The procedure of Example I was repeated using the same "batch" from which the tapes of Example I were prepared, except about 72 hours after aging of the composition. The aging would be expected to "uniformly" increase the holding power (duration) of each of the samples. The results are shown in Table III. Additionally, Table III includes the results of a fourth adhesive prepared from the same batch, and identical to III except that IV (like I) did not include filler and milling.

TABLE III

Group	Hrs. Duration of Holding Power Sample (1)	Sample (2)
I	144(+)	144(+)
II	8	$8\frac{1}{2}$(+)*
III	7	$8\frac{1}{2}$(+)*
IV	8(+)**	8(+)**

*: Fell during the night; at least less than 23.5 hrs.

**: Fell during the night; at least less than 71.5 hrs.

From each of Tables II and III, it is clear that the Group I pressure sensitive tapes grossly exceed the holding power of either of the tapes of Group II, III and IV. Although a minor improvement of Group I over each of Groups II and III could have been expected as a result of the milling-in of the aluminum hydrate filler of the Groups II & III, the marked superiority of Group I is unexpected. However, regardless as to the reason for the good results of Group III, the Group III does not include filler material and does not require the milling of the elastomer (pale crepe rubber).

Also in a comparison of Groups II and III of each of Tables II and III, it is noted that the Group II (which did *not* include material reactive with isocyanate) improved upon aging—as illustrated in Table III, as compared to Group III which included the amine compound which is reactive with isocyanate.

WHAT WE CLAIM IS:—

1. A pressure sensitive adhesive tape comprising a backing tape having coated on at least one face thereof an adhesive composition comprising an elastomer having a viscosity of from 40—100 Mooney, and a resinous composition including a major amount of high-melting point resin melting at least above 105°C and a minor amount of a low-melting point resin melting at most below 75°C, and a filler, characterized in that there is included from $\frac{1}{2}$—5% of an iocyanate based on the weight of the elastomer, the ratio of the high melting point resin to the low melting point resin being from 8/1 to 3/1 and the adhesive composition is substantially free of a material highly reactive with the isocyanate.

2. A pressure sensitive tape as recited in claim 1, wherein the resinous composition includes a terpene resin, a petroleum-derived resin, or a resin derived from hydrogenated wood rosin, as the high melting point resin or the low melting point resin.

3. A pressure sensitive tape as claimed in claim 1 and substantially as herein described.

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